

CORRECTED VERSION

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
5 February 2004 (05.02.2004)

PCT

(10) International Publication Number
WO 2004/011561 A1

(51) International Patent Classification⁷: C09D 11/00,
C09B 45/14, 45/16, 45/18, 45/20

(21) International Application Number:
PCT/GB2003/002117

(22) International Filing Date: 16 May 2003 (16.05.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0217446.4 27 July 2002 (27.07.2002) GB
60/410,810 16 September 2002 (16.09.2002) US

(71) Applicant (for US only): AVECIA LIMITED [GB/GB];
Hexagon House, Blackley, Manchester M9 8ZS (GB).

(72) Inventor; and

(75) Inventor/Applicant (for US only): WRIGHT, Gavin
[GB/GB]; PO Box 42, Hexagon House, Blackley, Man-
chester M9 8ZS (GB).

(74) Agents: MAYALL, John et al.; Avecia Limited, Intellec-
tual Property Group, PO Box 42, Hexagon House, Black-
ley, Manchester M9 8ZS (GB).

(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD,
SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US,
UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

(48) Date of publication of this corrected version:

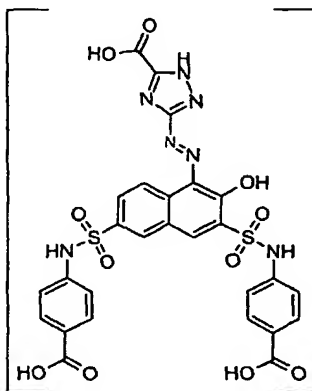
3 June 2004

(15) Information about Correction:

see PCT Gazette No. 23/2004 of 3 June 2004, Section II

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: INK



(I)

M

(57) Abstract: An ink comprising: (c) a metal chelate compound of Formula (I) or salt thereof, wherein M is nickel; and (b) a liquid medium. The inks are useful for ink jet printers.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau

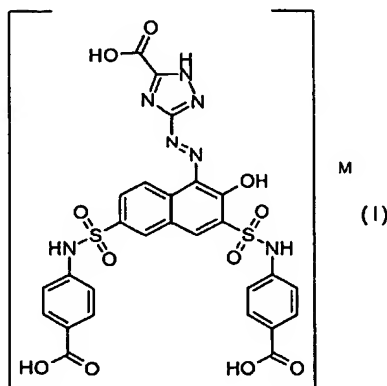


(43) International Publication Date
5 February 2004 (05.02.2004)

PCT

(10) International Publication Number
WO 2004/011561 A1

- (51) International Patent Classification⁷: C09D 11/00, C09B 45/14, 45/16, 45/18, 45/20
- (21) International Application Number: PCT/GB2003/002117
- (22) International Filing Date: 16 May 2003 (16.05.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
0217446.4 27 July 2002 (27.07.2002) GB
60/410,810 16 September 2002 (16.09.2002) US
- (71) Applicant (*for US only*): AVENCIA LIMITED
[GB/GB]; Hexagon House, Blackley, Manchester M9 8ZS (GB).
- (72) Inventor; and
- (75) Inventor/Applicant (*for US only*): WRIGHT, Gavin
[GB/GB]; PO Box 42, Hexagon House, Blackley, Manchester M9 8ZS (GB).
- (54) Title: INK
- (84) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



(57) Abstract: An ink comprising: (c) a metal chelate compound of Formula (I) or salt thereof, wherein M is nickel; and (b) a liquid medium. The inks are useful for ink jet printers.

WO 2004/011561 A1

INK

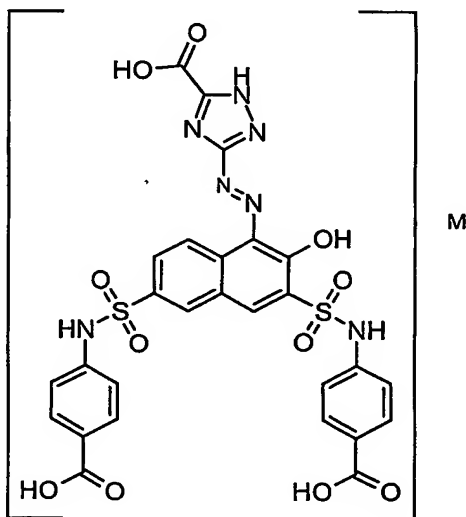
This invention relates to inks and to their use in ink jet printing ("IJP"). IJP is a non-impact printing technique in which droplets of ink are ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate.

There are many demanding performance requirements for inks used in IJP. For example they desirably provide sharp, non-feathered images having good water-fastness, light-fastness and optical density. The inks are often required to dry quickly when applied to a substrate to prevent smudging, but they should not form a crust over the tip of an ink jet nozzle because this will stop the printer from working. The inks should also be stable to storage over time without decomposing or forming a precipitate which could block the fine nozzle.

WO 01/48090 relates to metal chelate azo compounds which comprise a naphthol component and certain heterocyclic groups. WO 01/48090 does not disclose such compounds further substituted by a triazole ring for use in ink formulations.

According to a first aspect of the present invention there is provided an ink comprising:

(a) A metal chelate compound of Formula (1) or salt thereof, wherein M is nickel;



Formula (1)

and (b) a liquid medium.

It is especially preferred that the inks comprising the compound of Formula (1) are magenta in colour.

The inks comprising the compound of Formula (1) provide prints which exhibit a high light-fastness, good fastness to oxidising gases such as ozone and good optical density, particularly when used for ink jet printing. The inks according to the present

invention are also highly soluble which improves operability and reduces crusting and nozzle blockage when inks containing the compounds are used in an ink jet printer.

It is especially preferred that the compound of Formula (1) is in the form of a sodium, lithium, potassium, ammonium or substituted ammonium salt, because we have found that these salts provide prints which exhibit a high light-fastness when incorporated into an ink jet printing ink.

The metal chelate compound of Formula (1) or a salt thereof according to the present invention and the inks comprising the compound of Formula (1) also include tautomers thereof, especially tautomers of the triazole ring.

The compound of Formula (1) may be converted into a salt using known techniques. For example, an alkali metal salt of a compound may be converted into a salt with ammonia or an amine by dissolving an alkali metal salt of the dye in water and passing the solution through a column of a suitably modified ion exchange resin.

The inks according to the present invention may be, and preferably are, purified to remove undesirable impurities before they are incorporated into inks for ink jet printing. Conventional techniques may be employed for purification, for example ultrafiltration, reverse osmosis and/or dialysis.

The liquid medium preferably comprises:

- (i) water;
- (ii) a mixture of water and an organic solvent; or
- (iii) an organic solvent free from water.

The number of parts by weight of component (a) of the ink is preferably from 0.01 to 30, more preferably 0.1 to 20, especially from 0.5 to 15, and more especially from 1 to 5 parts. The number of parts by weight of component (b) is preferably from 99.99 to 70, more preferably from 99.9 to 80, especially from 99.5 to 85, and more especially from 99 to 95 parts. The number of parts of (a) + (b) is 100 and all parts mentioned herein are by weight.

Preferably component (a) is completely dissolved in component (b). Preferably component (a) has a solubility in component (b) at 20°C of at least 10%. This allows the preparation of concentrates which may be used to prepare more dilute inks and reduces the chance of the compound(s) of component (a) of the ink precipitating if evaporation of the liquid medium occurs during storage.

When the liquid medium comprises a mixture of water and an organic solvent, the weight ratio of water to organic solvent is preferably from 99:1 to 1:99, more preferably from 99:1 to 50:50 and especially from 95:5 to 80:20.

It is preferred that the organic solvent present in the mixture of water and organic solvent is a water-miscible organic solvent or a mixture of such solvents. Preferred water-miscible organic solvents include C₁₋₆-alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; ketones

and ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and diacetone alcohol; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, preferably diols having from 2 to 12 carbon atoms, for example pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and thiodiglycol
5 and oligo- and poly-alkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and 1,2,6-hexanetriol; mono-C₁₋₄-alkyl ethers of diols, preferably mono-C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy)ethoxy] ethanol, 2-[2-(2-ethoxyethoxy)
10 -ethoxy]-ethanol and ethyleneglycol monoallylether; cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone; cyclic esters, preferably caprolactone; sulphoxides, preferably dimethyl sulphoxide and sulpholane. Preferably the liquid medium comprises water and 2 or more, especially from 2 to 8, water-miscible organic solvents.

15 Especially preferred water-soluble organic solvents are cyclic amides, especially 2-pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone; diols, especially 1,5-pentane diol, ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol; and mono- C₁₋₄-alkyl and C₁₋₄-alkyl ethers of diols, more preferably mono- C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxy-2-ethoxy-2-ethoxyethanol.

20 When the liquid medium comprises an organic solvent free from water, (i.e. less than 1% water by weight) the solvent preferably has a boiling point of from 30° to 200°C, more preferably of from 40° to 150°C, especially from 50 to 125°C. The organic solvent may be water-immiscible, water-miscible or a mixture of such solvents. Preferred water-miscible organic solvents are any of the hereinbefore described water-miscible
25 organic solvents and mixtures thereof. Preferred water-immiscible solvents include, for example, aliphatic hydrocarbons; esters, preferably ethyl acetate; chlorinated hydrocarbons, preferably CH₂Cl₂; and ethers, preferably diethyl ether; and mixtures thereof.

30 When the liquid medium comprises a water-immiscible organic solvent, preferably a polar solvent is included because this enhances solubility of the metal chelate compound in the liquid medium. Examples of polar solvents include C₁₋₄-alcohols. In view of the foregoing preferences it is especially preferred that where the liquid medium is an organic solvent free from water it comprises a ketone (especially methyl ethyl ketone) and/or an alcohol (especially a C₁₋₄-alkanol, such as ethanol or propanol).

35 The organic solvent free from water may be a single organic solvent or a mixture of two or more organic solvents. It is preferred that when the medium is an organic solvent free from water it is a mixture of 2 to 5 different organic solvents. This allows a medium to be selected which gives good control over the drying characteristics and storage stability of the ink.

Ink media comprising an organic solvent free from water are particularly useful where fast drying times are required and particularly when printing onto hydrophobic and non-absorbent substrates, for example plastics, metal and glass.

An especially preferred ink comprises:

- 5 (i) 1 to 10 parts in total of the compound of Formula (1) or salt thereof;
(ii) 2 to 60, more preferably 5 to 40 parts of water-soluble organic solvent; and
(iii) 30 to 97, more preferably 40 to 85 parts water;

wherein all parts are by weight and the sum of the parts (i) + (ii) + (iii) = 100.

10 When the liquid medium in the ink comprises a mixture of water and an organic solvent; or an organic solvent free from water, component (i) of the ink may comprise a compound of the Formula (1) or salt thereof, as hereinbefore defined.

15 Preferred low melting solid media have a melting point in the range from 60°C to 125°C. Suitable low melting point solids include long chain fatty acids or alcohols, preferably those with C₁₈₋₂₄ chains, and sulphonamides. A compound of Formula (1) may be dissolved in the low melting point solid or may be finely dispersed in it.

The inks according to the present invention may also contain additional components conventionally used in ink jet printing inks, for example viscosity and surface tension modifiers, corrosion inhibitors, biocides, fogation reducing additives, anti-cockle agents to reduce paper curling and surfactants which may be ionic or non-ionic.

20 The pH of the ink is preferably from 4 to 11, more preferably from 7 to 10.

The viscosity of the ink at 25°C is preferably less than 50cP, more preferably less than 20 cP and especially less than 5cP.

25 A second aspect of the present invention provides a process for printing an image on a substrate comprising applying thereto by means of an ink jet printer an ink according to the first aspect of the present invention. The preferences for the ink used in this process are as hereinbefore defined in relation to the first aspect of the present invention.

30 The ink jet printer preferably applies the ink to the substrate in the form of droplets which are ejected through a small orifice onto the substrate. Preferred ink jet printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the orifice, thereby causing the ink to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink jet printers the oscillation of a small crystal causes ejection of the ink from the orifice.

35 The substrate is preferably paper, plastic, a textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain or treated papers which may have an acid, alkaline or neutral character. Examples of commercially available papers include, HP Premium Coated Paper, HP Photopaper (all available from Hewlett Packard Inc.), Stylus Pro 720

dpi Coated Paper, Epson Photo Quality Glossy Film, Epson Photo Quality Glossy Paper (available from Seiko Epson Corp.), Canon HR 101 High Resolution Paper, Canon GP 201 Glossy Paper, Canon HG 101 High Gloss Film (all available from Canon Inc.), Wiggins Conqueror paper (available from Wiggins Teape Ltd), Xerox Acid Paper and Xerox Alkaline paper, Xerox Acid Paper (available from Xerox).

A third aspect of the present invention provides a substrate, preferably a paper, an overhead projector slide or a textile material, printed with an ink according to the first aspect of the present invention or by means of the process according to the second aspect of the present invention.

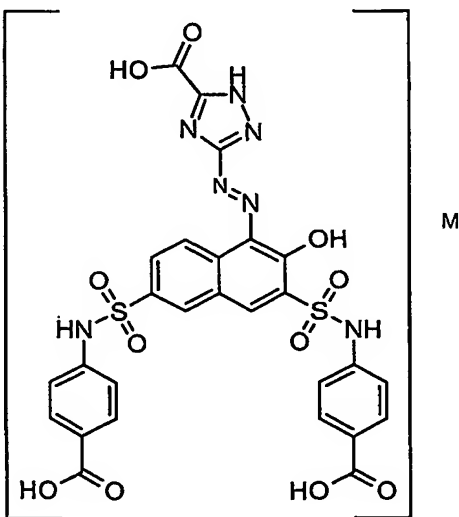
According to a fourth aspect of the present invention there is provided an ink jet printer cartridge comprising a chamber and ink, wherein the ink is present in the chamber and the ink is as defined in the first aspect of the present invention.

According to a fifth aspect of the present invention there is provided an ink jet printer containing an ink jet printer cartridge, wherein the ink jet printer cartridge is as defined in the fourth aspect of the present invention.

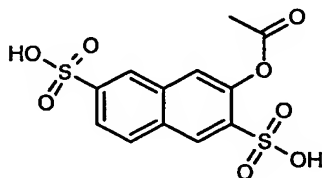
The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless specified otherwise.

Example 1

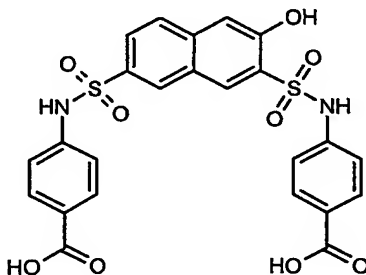
Compound (1) wherein M is nickel



Compound (1)

Stage (a): Preparation of 2-acetoxynaphthalene-3,6-disulphonic acid

5 Acetic anhydride (350 ml, 3.8mol) was added dropwise to a suspension of 2-hydroxynaphthalene-3,6-disulphonic acid di sodium salt (87g, 0.25mol) in *N,N*-dimethylacetamide (350ml). The reaction mixture was stirred at 125°C for 24 hours, cooled to room temperature and added to acetone (2500ml). The product was filtered off, washed with acetone (3 x 100ml) and dried to give 95.2g of a cream coloured solid.

Stage (b): Preparation of 3,6-bis-(4-carboxy-phenylsulfamoyl)-2-hydroxy-naphthalene

15 POCl_3 (50ml, 0.538mol) was added dropwise to a suspension of the product from stage (a) (50g, 0.128mol) in acetonitrile (250ml) at reflux. The reaction mixture was stirred for 3 hours at 70°C, cooled, added to ice / water (4000ml) and the naphthalene disulfonyl chloride extracted with dichloromethane (4 x 300ml). The combined extracts were dried with MgSO_4 , evaporated under reduced pressure and the residue dissolved in *N,N*-dimethylacetamide (400 ml). 4-Aminobenzoic acid (34.3g, 0.25mol) was added to the above solution, the reaction mixture was stirred overnight at room temperature and then added to water (3000ml). The pH was then lowered to 0.5 with concentrated H_2SO_4 and the precipitated product extracted from ethyl acetate (4 x 300ml). The combined extracts were washed with 1N HCl (600ml), dried with MgSO_4 and evaporated under reduced pressure. The residue was dissolved in water (1000ml) at pH 12 (2N NaOH) and then stirred for 1 hour at 50-60°C. The solution was allowed to cool, the pH lowered to pH 4 with concentrated HCl and the product filtered off and dried to give 41.5g (53% yield) of a tan coloured solid.

Stage (c):

3-amino-1,2,4-triazole-5-carboxylic acid hydrate (1.28g, 0.01mol) was suspended in water (50ml) and dissolved by the addition of 2M NaOH to pH 8. Sodium nitrite (0.76g, 0.011mol) was added and the solution stirred until the sodium nitrite had dissolved.

5 The mixture was then added dropwise to a cooled mix of ice-water (30g) and concentrated HCl (3.0ml) at 0-5°C, the mixture was stirred for 30 minutes. at 0-5°C and then excess nitrous acid was removed by adding sulphamic acid. The diazo suspension was added slowly to a solution of the product from stage (b) (5.42g, 0.01mol) in water (100ml) at pH 7-8 (2N NaOH) cooled below 5 °C. The reaction mixture was then stirred at
10 0-5°C for one further hour, the product was precipitated by acidification to pH 4 with 2N HCl and collected by filtration. The product was then washed with water and dried in a vacuum desiccator to give 6.4g of an orange solid.

Stage (d): Preparation of Compound (1)

15 A solution of nickel acetate tetrahydrate (1.38g, 0.0055mol) in water (10ml) was added dropwise to the product from stage (c) (5.0g, 0.0073mol) dissolved in water (100ml) at pH 7 (2N NaOH). The reaction mixture was stirred for 2 hours at ambient temperature, dialysed using SpectraPor membrane tubing (molecular weight cut off 3500) to low conductivity (<100µs). The product was obtained by evaporation under reduced
20 pressure to afford a dark crystalline solid (6g). Analysis by mass spectrometry found m/z 1419. Requires M⁺ = 1420.

Example 2 - Inks

25 The inks described in Tables I and II may be prepared wherein the Compound described in the first column is the Compound made in Example 1. Numbers quoted in the second column onwards refer to the number of parts of the relevant ingredient and all parts are by weight. The inks may be applied to paper by thermal or piezo ink jet printing.

The following abbreviations are used in Table I and II:

30 PG = propylene glycol
DEG = diethylene glycol
NMP = N-methyl pyrrolidone
DMK = dimethylketone
IPA = isopropanol
35 MEOH = methanol
2P = 2-pyrrolidone
MIBK = methylisobutyl ketone
P12 = propane-1,2-diol
BDL = butane-2,3-diol

CET= cetyl ammonium bromide

PHO = Na_2HPO_4 and

TBT = tertiary butanol

TDG = thiodiglycol

TABLE I

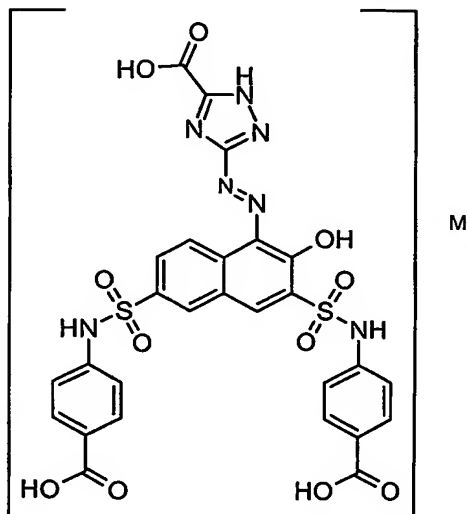
Compound	Dye Content	Water	PG	DEG	NMP	DMK	NaOH	Na Stearate	IPA	MEOH	2P	MIBK
1	2.0	80	5		6	4					5	
1	3.0	90		5	5		0.2					
1	10.0	85	3		3	3				5	1	
1	2.1	91		8								1
1	3.1	86	5					0.2	4			5
1	1.1	81			9		0.5				9	
1	2.5	60	4	15	3	3			6	10	5	4
1	5	65		20					10			
1	2.4	75	5	4		5				6		5
1	4.1	80	3	5	2	10		0.3				
1	3.2	65		5	4	6			5	4	6	5
1	5.1	96								4		
1	10.8	90	5						5			
1	10.0	80	2	6	2	5			1		4	
1	1.8	80		5							15	
1	2.6	84			11						5	
1	3.3	80	2			10				2		6
1	12.0	90				7	0.3		3			
1	5.4	69	2	20	2	1					3	3
1	6.0	91			4						5	

TABLE II

Compound	Dye Content	Water	PG	DEG	NMP	CET	TBT	TDG	BDL	PHO	2P	PI2
1	3.0	80	15			0.2					5	
1	9.0	90		5						1.2		5
1	1.5	85	5	5		0.15	5.0	0.2		0.12		
1	2.5	90		6	4							6
1	3.1	82	4	8		0.3				0.2		
1	0.9	85		10					5			
1	8.0	90		5	5			0.3				
1	4.0	70		10	4				1		4	11
1	2.2	75	4	10	3				2		6	
1	10.0	91			6						3	
1	9.0	76		9	7		3.0			0.95	5	
1	5.0	78	5	11							6	
1	5.4	86			7						7	
1	2.1	70	5	5	5	0.1	0.2	0.1	5	0.1	5	
1	2.0	90		10								
1	2	88						10				
1	5	78			5			12			5	
1	8	70	2		8			15			5	
1	10	80						8			12	
1	10	80		10								

CLAIMS

1. An ink comprising:
(a) a metal chelate compound of Formula (1) or salt thereof, wherein M is nickel;



Formula (1)

and (b) a liquid medium.

2. An ink according to claim 1 wherein the liquid medium comprises a mixture of water and an organic solvent.

3. An ink according to claim 1 or 2 comprising
(i) 1 to 10 parts of the compound of Formula (1) or salt thereof;
(ii) 2 to 60 parts of water-soluble organic solvent; and
(iii) 30 to 97 parts water;
wherein all parts are by weight and the sum of parts (i) + (ii) + (iii) = 100.

4. A process for printing an image on a substrate comprising applying thereto by means of an ink jet printer an ink according to any one of claims 1 to 3.

5. A substrate printed with an ink according to any one of claims 1 to 3, or by means of the process according to claim 4.

6. An ink jet printer cartridge comprising a chamber and ink, wherein the ink is present in the chamber and the ink is as defined in any one of claims 1 to 3.

7. An ink jet printer containing an ink jet printer cartridge, wherein the ink jet printer cartridge is as defined in claim 6.
8. An ink substantially as herein described with reference to any of the examples.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/GB/02/117

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09D11/00 C09B45/14 C09B45/16 C09B45/18 C09B45/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, A	EP 1 270 676 A (MITSUBISHI CHEM CORP) 2 January 2003 (2003-01-02) paragraphs '0018!', '0039!'; claims 1-22; figure L1; examples; tables 1,2,7,9	1-8
Y	CHEMICAL ABSTRACTS, vol. 97, no. 10, 6 September 1982 (1982-09-06) Columbus, Ohio, US; abstract no. 73900, HIRSCH BODO ET AL: "some new dyes based on 3-amino-1,2,4-triazole derivatives" XP009016260 abstract & SBORNIK VEDECKYCH PRACI-VYSOKA SKOLA CHEMICKOTECHNOLOGICKA PARDUBICE, vol. 44, 1981, pages 285-90, -/--	1



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- * & * document member of the same patent family

Date of the actual completion of the international search

9 September 2003

Date of mailing of the international search report

15/09/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Frison, C

INTERNATIONAL SEARCH REPORT

Internal Application No

PCT/8/02117

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>CHEMICAL ABSTRACTS, vol. 76, no. 14, 3 April 1972 (1972-04-03) Columbus, Ohio, US; abstract no. 80560, YUSUPOV M. YU. ET AL: "synthesis of azo compounds based on aminotriazolecarboxylic acid and some of their analytical characteristics" XP009016502 abstract & DOKLADY AKADEMII NAUK TADZHIKSKOI SSR, vol. 14, no. 9, 1971, pages 31-3, -----</p>	1

INTERNATIONAL SEARCH REPORT

Internal Application No

PCT/GB 03/02117

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1270676 A	02-01-2003	JP 2003096323 A	03-04-2003
		EP 1270676 A1	02-01-2003
		US 2003125530 A1	03-07-2003
